

THE ROLE OF RADIOGENIC HEAT IN MATURATION OF ORGANIC MATTER WITHIN OIL SHALES OF DUWI FORMATION IN QUSEIR-SAFAGA DISTRICT, RED SEA COASTAL AREA, EGYPT

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تأثير الحرارة الناتجة من الاشعاع على نضوج المادة العضوية
في صخور الطفلة الزيتية لتكوين «ضوي» في منطقة القصير - سفاجا
على ساحل البحر الأحمر - بمصر

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تحتوي صخور الطفلة الزيتية في تكوين «ضوي» بمنطقة القصير - سفاجا بمصر على نسبة كبيرة من الكيروجين السابروبيلي لمجموعة «الليبتينيت» ذات الأصل البحري. ويدل التحليل الكيميائي أن هذا الكيروجين يتبع النوع I والنوع II غير الناضج والواقع في نطاق مرحلة الدايا جينيسيز لنضوج المادة العضوية. وقد أوضحت الدراسة أن الحرارة الناتجة من عنصر اليورانيوم المشع في صخور الفوسفات بتكوين «ضوي» قد ساعدت على ارتفاع قيمة انعكاس الفيترينيت في الكيروجين داخل صخور الطفلة الزيتية الى المستوى المميز لمرحلة الكاتاجينيسيز لنضوج المادة العضوية.

Keywords: Radiogenic heat, maturation, organic matter, oil shales, Quseir, Safaga, Red Sea, Egypt.

ABSTRACT

The oil shale beds of Duwi Formation at Quseir-Safaga district in Egypt show a high content of organic matter (kerogen) and a fair pyrolysis oil yield. Kerogens of these rocks are composed mainly of marine amorphous and structured sapropelic liptinitic phytoclasts of algae with minor contribution of the humic materials. Also, these kerogens belong to the immature types I and II which are buried in the diagenesis stage of maturation. Although these kerogens are immature they show high vitrinite reflectances (up to 0.7 %) comparable with the catagenesis stage of maturation. The study of uranium contents of phosphorites within Duwi Formation indicates that the produced radiogenic heat of the uranium mass markedly contribute to the maturity level of the organic matter of oil shales. This explains presence of the high vitrinite reflectances which correspond to the temperature limits of the catagenesis stage.

INTRODUCTION

The oil shale rocks contain varying amounts of organic materials in the form of kerogen, which upon heating yields hydrocarbon compounds (shale oil). In Egypt, a notable feature in the Upper Cretaceous-Lower Tertiary sedimentary succession is the presence of thick shale beds (Quseir Variegated Shale, Dakhla Shale, and Esna Shale) below and above the phosphate beds of Duwi Formation. The productive phosphate occurrences belong to the middle facial zone stretching in Quseir-Safaga district along the Red Sea coast, Abu Tartur plateau in the Western Desert, and El Sebaiya and east Luxor along the Nile Valley. A remarkable oil shale bed has been reported in several localities along the regional extension of Duwi Formation. This feature applies not only for Egypt but also for the whole North-African phosphate belt, where similar oil shale occurrences are known in Morocco and Tunisia, extending eastward to Palestine, Jordan, and Syria.

The present work aims mainly to develop a genetic model for the evaluation of the organic matter in the phosphate - oil shale association in Quseir-Safaga phosphate district (Fig. 1). Also, this study concerns with the source heat which acts on the organic matter in Duwi Formation.

GEOLOGY

Lithologically, Duwi Formation consists of intercalations of phosphorites, shale, marl, and thin chert beds in Quseir-Safaga district. It shows some lateral and vertical lithological changes, thus complicating lithostratigraphic correlation of the phosphate horizons. Duwi Formation belongs to the Late Campanian — Early Maastrichtian age. Stratigraphically, this formation overlies the Quseir Variegated Shale and underlies the Dakhla Shale in the studied area (Fig. 2).

OIL SHALE BEDS

Geology and geochemistry of oil shale beds in Quseir-Safaga district were studied by many investigators. Malak et al. [1], Darwish [2], Ganz [3], Troger [4], Abdel Rahman and Khaled [5], Khaled et al. [6], El Kammar et al [7], Khaled [8-11] are among. These studies indicate that there could be a total amount of over 200 million tons of the black oil shales having combustible material content

ranges from 23 to 48 wt. % [5]. Also, the Fischer assay oil yield of them measures up to 45 US gallon per ton and the gas content is 3% at the average [4]. According to Khaled [8-11] the measured total organic carbon content values of these oil shale beds range from 7.7 to 16.8 wt. %. Also, their kerogens are mainly composed of autochthonous liptinite group including marine amorphous and structured sapropelic phytoclasts of algae (alginite). The liptinites are mixed with less abundant humic materials (herbaceous) which are mainly formed of autochthonous vitrinite (first cycle) and inertinite maceral groups. These kerogens belong to the immature type I in Safaga oil shales and type II in Hamrawein and Quseir rocks. The elemental analysis, Infrared, and Thermogravimetric curves (TGA and DTG) of kerogens and pyrolysis results (both Rock-eval and Curie-point techniques) of the whole rock samples show that these oil shale beds were buried in the diagenesis stage of maturation. In addition, Hamrawein oil shales show higher maturity level since their kerogen is located almost at the boundary between diagenesis and catagenesis zones (Fig. 3).

The measured vitrinite reflectance (R^o , %) ranges from 0.3 to 0.7%, the latter value characterizes Hamrawein oil shales [8]. The higher values ($>0.5\%$) indicate that the organic matter was affected by a high temperature (T) due to a heat quantity which is not comparable with the physicochemical conditions, particularly depth and temperature range ($T < 60^\circ\text{C}$) characterizing the diagenesis stage [12], Fig. 5. These high reflectances suggest the conditions of the catagenesis stage of maturation ($R^o > 0.5\%$, and $T > 65^\circ\text{C}$) although these oil shales have not reached this stage yet. Also, Troger [4] recorded high R^o values (from 0.8 to 1.1%) and attributed them to the strong influence of the high sun temperature on the core samples he studied.

The present study is a trial to indicate a correlation between maturity level of the organic matter in oil shales and the radioactivity level of the surrounding phosphate rocks, where uranium is an important potential source of radiogenic heat contributing to the maturation process of kerogen.

GEOCHEMICAL ASPECT

Uranium is generally concentrated in marine phosphorites which therefore are considered as one of its important

sources (Altschuler et al. [13]; Kolodny and Kaplan [14]; Fench et al. [15]; Burnett [16]; Burnett and Gombert [17]. Uranium is removed from aqueous solutions by precipitation in reducing environments such as anoxic sedimentary basins; across redox boundaries in pyritic or organic-rich sediments; by absorption on clays, and by sorption on, and complexing with, humic organic matter and iron hydroxides. Phosphatic sediments derived their uranium from sea water through the ability of the element to form phosphate complexes, such as $(\text{UO}_2\text{HPO}_4)_2^{2-}$, in water of relatively high pH. Uranium occurs in phosphorites in two oxidation states: as reduced tetravalent U^{4+} and oxidized hexavalent U^{6+} [18]. In sea water, dissolved U is present in the hexavalent state mainly as uranyl ions. Meanwhile, in strongly reducing marine sediments, however, U is precipitated as insoluble phases of tetravalent state [9]. The exact mechanism of U enrichment in organic-rich sediments is still uncertain. Some of the suggested mechanisms are summarized by Abdel Rahman [20] as follows:

1) adsorption and complexation of U by the organic matter under reducing conditions either in the water column [21] or within the sediment [22].

2) selective uptake of U by marine apatite forming authigenically within organic-rich [23, 24]. A different approach to the emplacement of U into phosphorites was pointed out by Arrhenius [25] who cited that bones are built mainly of hydroxyapatite and are uranium free.

Since the mid of the present century, several studies on the U in Egyptian phosphorites have been published. Among them are those by Hussein [26], Rittman and Machu [27], Hegazy and Hussein [28], Zaghoul and Mabrouk [29], El Kammar [30], Hassan and El Kammar [31], Hussein and EL Kassas [32, 33], Dabous [34], El Kammar and El Reedy [35], Tamish [36], and Hussein [37]. In general, most phosphorite deposits contain between 10 and 60ppm U, but some are enriched to 2500 ppm or more [13]. Vast tonnages at grades of over 100 ppm U occur in the North-African belt of phosphorites. In Egypt, very low concentrations of U are measured in the oil shale rocks, especially in Quseir-Safaga phosphate mines. On the other side, phosphate beds in the study area show relatively higher concentrations of U (up to 142 ppm) measuring an average value of 76.78 ppm (Table 1).

NATURAL RADIOACTIVITY AND RADIOGENIC HEAT

Uranium (U), thorium (Th), and potassium (K) are responsible for the natural heat generation of the Earth. The amount of heat generated by one gram (gm) of each of these three radioactive elements in secular equilibrium with their decay products is 0.73, 0.2, and 2.7×10^{-5} calories (cal) per gm per year (y), respectively. The presence of high levels of these heat producing elements in phosphate rocks and black shales is attributed in considering them as potential "hot rocks" radiogenic heat sources. From the geological point of view, U is of greater significance than either Th or K. This is because U contributes more radioactivity weight for weight than the other two elements, and also because the hexavalent U is extremely mobile under oxidizing conditions, especially in acid or carbonate-rich waters. Also, U is mobile as colloidal particles or as organic complexes. Under reducing conditions, however, it is strongly sorbed by organic substances and iron sulphides. Its mobility or stability depending on Eh/pH conditions is of special importance to the distribution of radioelements in the sedimentary layers. However, the rate of radiogenic heat production in the Earth at present equals 1.590×10^{20} cal/y. This would correspond to a heat flux through the Earth's surface of 31.176 cal/cm²/y. Also, the terrestrial heat flux in contents measures 46.04 cal/cm²/y. The average rate of radiogenic heat production during the past 450 million years (m.y) was 15% greater than the present rate, i.e. it was 1.8×10^{20} cal/y. Meanwhile, during the past 65 m.y it was 2 % greater than the present, i.e. it equals 1.622×10^{20} cal/y [38].

In Quseir-Safaga district the previous investigations indicate that, the estimated reserve of phosphorites equals about 100 million tons [39] while that of oil shales is about 166 million tons [5]. Also, the quantity of U in phosphorites measures about 76.7×10^5 kg.

The radiogenic heat production due to the U mass in Duwi Formation is given by:

$$Q_u = mxR$$

where:

m is the mass (kg) and R is the rate of heat production of

u (730 cal/kg/y)

$$\therefore Q_u = 76.78 \times 10^5 \times 730 = 5.6 \times 10^9 \text{ cal/y}$$

Then, the total amount of heat produced by U through the entire geologic age (65 million years) of phosphorites (from Maastrichtian to the present time) will be:

$$Q_u \text{ (total)} = 5.6 \times 10^9 \times 65 \times 10^6 = 3.64 \times 10^{17} \text{ cal}$$

Using the mass of phosphorite and oil shale rocks in the area (266 million tons), the specific heat of them (170 cal/kg), and the initial temperature (T_1) prevailed during deposition of these rocks (15°C) and the average value of their present temperature ($T_2 = 40^\circ\text{C}$), the amount of heat capacity of these rocks in the area is given by:

$$Q = m \times S \times \Delta T$$

where:

m is the mass of an object (kg)

S is the specific heat of the object (cal/kg°C) and

ΔT is the temperature difference between T_1 (the initial temperature) and T_2 (the final temperature) of the object.

$$\therefore Q_{\text{rocks}} = 266 \times 10^9 \times 170 \times (40-15) = 1.131 \times 10^{15} \text{ cal}$$

This amount of heat capacity of rocks is smaller than radiogenic heat production of U (3.64×10^{17} cal) through the entire geologic age of these rocks (65 million years).

Assuming that, the produced radiogenic heat is completely absorbed by these rocks in Duwi Formation or transferred through them, so the increase of temperature of the rocks is:

$$\begin{aligned} Q_u &= m \times S \times \Delta T \\ 5.6 \times 10^9 &= 266 \times 10^9 \times 170 \times \Delta T \\ \therefore \Delta T &= 0.00013 \text{ }^\circ\text{C per year} \end{aligned}$$

Accordingly, the increase in temperature through the entire geologic age of the rocks will be:

$$\text{Total increase in temperature} = 0.00013 \times 65 \times 10^6 = 8450 \text{ }^\circ\text{C}$$

Also, the quantity of heat required to raise the temperature of phosphorites and oil shales from 15 °C (the initial temperature) to 65 °C (the temperature value corresponds to the roof of the catagenesis of maturation) is given by:

$$\begin{aligned} Q \text{ (catagenesis)} &= m \times S \times \Delta T \\ &= 266 \times 10^9 \times 170 \times (65-15) = 2.261 \times 10^{15} \text{ cal} \end{aligned}$$

The above calculations indicate that U of Duwi Formation

has generated an amount of radiogenic heat (3.64×10^{17} cal) which is bigger than the amount of heat required to raise the temperature of phosphorites and oil shale rocks up to the temperature limit of the roof of the catagenesis stage of maturation.

Today, the internal heat of the Earth is believed to come from three sources: the residual heat of accumulation, continuing accretion of the core, and the decay of long-lived radioactive isotopes. Also, a loss of heat due to the heat transfer is acting continuously giving rise to decrease the temperature of rocks. In case of Duwi Formation in the studied area there is an addition heat resource due to the U content which compensates the rocks (particularly phosphorites and oil shales) for the heat they lose. This could interpret the presence of high vitrinite reflectances given by kerogen macerals of the studied oil shales in the area.

CONCLUSIONS

Duwi Formation in Quseir-Safaga district contains several phosphate and oil shale beds. Kerogens of oil shales are immature having the geochemical characteristics of the diagenesis stage of maturation. These kerogens show high vitrinite reflectances which correspond to the catagenesis stage. Presence of high uranium contents in the phosphorites resulted in the production of a significant amount of radiogenic heat which contributes to maturity level and vitrinite reflectances of the organic matter in the oil shale beds in the area.

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REFERENCES

- [1] Malak, E.K., E.R. Philobos, I.K. Abdou and M.M. Ashry, 1977. Some petrographical, mineralogical and organic geochemical characteristics of black shales from Quseir and Safaga, Red Sea area, Egypt. Desert Inst. Bull. A. R. E., 27: 1-15.

- [2] Darwish, M., 1984. Optimistic hydrocarbon potentialities of the oil shales in the Quseir-Safaga landstretch. *Egypt. Bull. Fac. Sci. Zagazig Univ.*, 6:107-117.
- [3] Ganz, H., 1984. Organic-geochemical and palynological studies of a Dakhla Shale profile in southern Egypt. Part B: Origin of the organic matter and its relation to phosphorite Formation. *Berliner Geowiss. Abh. (A)*, 50: 363-374.
- [4] Troger, U., 1984. The oil shale potential of Egypt. *Berliner Geowiss. Abh., (A)*, 50: 375-380.
- [5] Abdel Rahman, A. A. and K. A. Khaled, 1988. Preliminary evaluation of the Eastern Desert of Egypt. 3rd Cong. Chem., Engin., Cairo. *TESCE*, 14, 2 III: 169-184.
- [6] Khaled, K. A., A. R. Abdel Ghany, A. A. Abdel Rahman and A. M. El Fadly, 1989. Lateral variation of geochemical characteristics of some oil shale beds in Quseir-Safaga environs, Eastern Desert, Egypt. 2nd Intern. Conf. Min. Metall. Eng., Suez Canal Univ., Suez, 105-119.
- [7] El Kammar, A. M., M. Darwish, G. Philip, and M.M. El Kammar, 1990. Composition and origin of black shales from Quseir area, Red Sea, Egypt. *J. Univ. Kuwait (Science)*, 17: 177-190.
- [8] Khaled, K. A. 1992a. Organic petrology of Oil Shales in Quseir-Safaga district, Egypt. *Qatar Univ. Sci. J., Qatar*, 12:176-184.
- [9] Khaled, K. A., 1992b. Physicochemical studies on Upper Cretaceous oil shales in Hamrawein phosphate mines, Eastern Desert, Egypt, *Egypt Soc. Eng., Soc. Chemical Eng., Cairo, TESCE*, 18:57-85.
- [10] Khaled, K. A., 1996. Organic Geochemistry of Late Cretaceous oil shales of Duwi Formation in Quseir phosphate mines, west of the Red Sea, Egypt. *Geol. Soc. Egypt. Spec. Publ.*, 2 (in press).
- [11] Khaled, K. A., 1997. On the nature of kerogen in oil shale beds of Safaga phosphate mines, Red Sea, Egypt. 3rd Conf. Geochemistry, Univ. Alexandria, Egypt., III: 1-18.
- [12] Merriman, D., S. Kemp, and N. Smith, 1995. Clay Minerals and Hydrocarbons. *Earthwise, British Geological Survey, Issue 7, Sept. 1995*, p.31.
- [13] Altschuler, Z. S., 1980. The geochemistry of trace elements in marine phosphorites. Part I: Characteristics abundance and enrichment. *SEPM Spec. Publ.*, 29:19-30.
- [14] Kolodny, Y. and I. R. Kaplan, 1970. Uranium isotopes in sea-floor phosphorites. *Geochem. Cosmochim. Acta.*, 34: 3-24.
- [15] Fench, W. I., A. P. Butler, F. C. Armstrong, and A. E. Weissenborn, 1973. Nuclear fuels-Uranium. *U. S. Geol. Surv. Prof. Paper*, 820: 456-468.
- [16] Burnett. W. C., 1974. Phosphorite deposits from the sea floor of Peru and Chile: Radiochemical and investigations concerning their origin. Ph.D. Thesis, Hawaii Univ., 164 p.
- [17] Burnett. W. C., and D. N. Gomberg, 1977. Uranium oxidation and probable subaerial weathering of phosphatized limestones from the Pourtales Terrace. *Sedimentology*, 24: 291-302.
- [18] Kolodny, Y. 1981. Phosphorites. in: Emilinat, C (ed.) *The Sea*, 7:981-1023. Wiley, New York.
- [19] Kolodny, Y. and I. R. Kaplan, 1973. Deposition of Uranium in the sediment and interstitial water of an anoxic fjord. *Proc. Symp. Hydrogeoch. and Biogeochem.*, Tokyo, 1:418-442.
- [20] Abdel Rahman, M., 1992. Geochemical, mineralogical and sedimentological studies on phosphorites of the Nile Valley (Duwi Formation) between Qena and Idfu, Egypt. Ph. D. Thesis, Technischen Univ. Berlin, 173 p.

- [21] Koczy, F.F., F. Tomic, and F. Hecht, 1957. Zur geochemie des urans in Ostseebechen. *Geochim. Cosmochim. Acta.*, 11:86-102.
- [22] Manheim, F. T., 1961. A geochemical profile in the Baltic Sea. *Geochim. Cosmochim. Acta.*, 25:52-70.
- [23] Altschuler, Z. S., R. S Clarke, and E. J., Young, 1958. Geochemistry of uranium in apatite and phosphorite. U. S. Geol. Surv. Prof. Paper, 314-D: 45-87.
- [24] Baturin, G. N., A. V. Kochenov, and Yu. M. Senin, 1971. Uranium concentration in recent ocean sediments in zones of rising currents. *Geochem. Intern.*, 8 (1): 281-286.
- [25] Arrhenius, G., 1963. Pelagic sediments. In: Hill, M. N. (ed) *The Sea*, 3:655-727. Wiley, New York.
- [26] Hussein H. A., 1954. Studies on some Egyptian phosphates with special reference to their radioactivity. M.Sc. Thesis, Alexandria Univ., Egypt.
- [27] Rittman, A. and W. Machu, 1955. On the origin of the Egyptian phosphate deposits. *Bull. Fac. Eng., Cairo Univ.*, 3:300-318.
- [28] Hegazy, R. and H. A. Hussein, 1955. Remarks on the uranium content of some black shales and phosphates from Kosseir and Safaga. *Proc. Egypt. Acad. Sci., Cairo*, 11:63-66.
- [29] Zaghloul, Z. M. and B. Mabrouk, 1964. On uranium in Dakhla and Mahamid phosphate deposits. *J. Geol. Egypt*, 8:79-87.
- [30] El Kammar, A. M., 1974. Comparative mineralogical and geochemical study on some Egyptian phosphorites from Nile Valley, Quseir area and Kharga Oasis, Ph.D. Thesis, Cairo Univ., 425p.
- [31] Hassan, F. and A. M. El Kammar, 1975. Environmental conditions affecting the distribution of uranium and rare earth elements in Egyptian phosphorites. *Egypt. J. Geol.*, 19:169-178.
- [32] Hussein H. A. and I. A. El Kassas, 1980. Some favourable host rocks for uranium and thorium mineralization in Central Eastern Desert of Egypt. *Annals of the Geological Society of Egypt*, Vol. X:897-908.
- [33] Hussein H. A. and I. A. El Kassas, 1983. Uranium resources in the Arab Republic of Egypt. *Transactions of the Arab Mining and Petroleum Associations, Cairo, Egypt*, XXXIX: Paper No.2/1, 14p. (in Arabic).
- [34] Dabous, A. A. 1981. Mineralogy, geochemistry and radioactivity of some Egyptian phosphorite deposits. Ph.D. Thesis, Florida State Univ., 201 p.
- [35] El Kammar, A. M. and M. W. El Reedy, 1984. Geochemistry of Uranium and some rare earth elements in the Cretaceous-Tertiary sediments of Abu Tartur, Western Desert, Egypt. *Annals Geol. Surv. Egypt*, XIV:75-86.
- [36] Tamish, M., 1988. Geomathematical and geochemical studies on Egyptian phosphorites deposits. Ph. D. Thesis, Berlin Geowiss. Abh., (A) 98:97 p.
- [37] Hussein H. A., 1992. Uranium and rare earth elements in Egyptian phosphorites, Egypt. *Arab Soc. Min. Petrol., Seminar on phosphates industry in Egypt, Cairo*, 3:6 p (in Arabic).
- [38] Emiliani, C., 1995. *Planet Earth*. Cambriage Univ. Press. 324 p.
- [39] Beshai, A. H., 1992. The Egyptian phosphorites. *Arab Soc. Min. Petrol., Sem. phosphate industry in Egypt. Cairo*, 1: 6 p (in Arabic).

**Table 1. : Uranium Content (ppm) of phosphorites
in some mines, Quseir - Safage District.**

Area	Mine Name	U, ppm
I. Quseir	Hammadat	55
	Abu Tundub	90
	Abu Shgeila	100
	Wadi El Hamra	80
	Wadi Um Elqueh	72
	Younes	80
	Gebel Duwi	19
	”	133
	Nasser	13
	”	52
	”	50
	”	40
	”	72
II. Hamrawein	Hamrawein A & B	95
	>>	142
	>>	120
	>>	126
	>>	46
	>>	48
III. Safaga	Um Hueitat	80
	”	90
	Rabah	90
	Wasif	76
Average		76.78 ppm

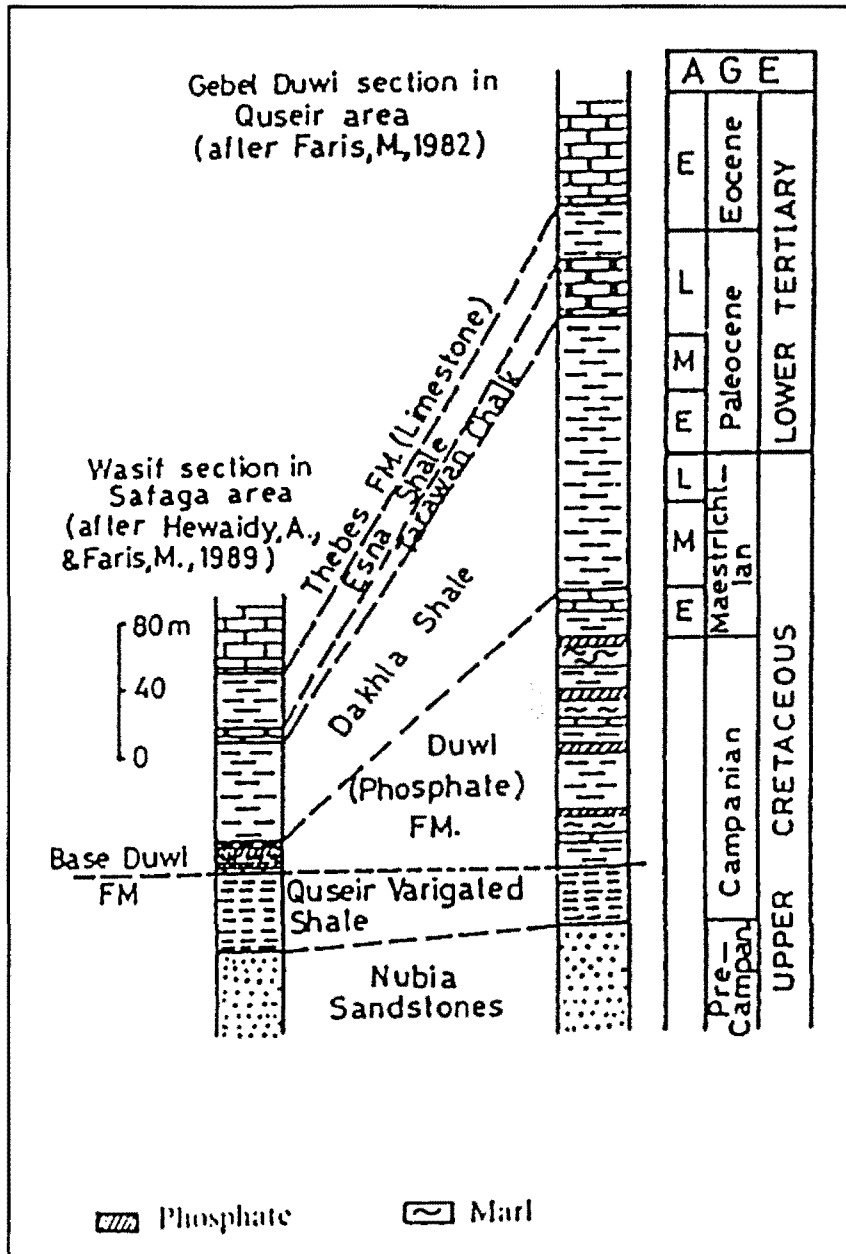


Fig. 2. Stratigraphic sections of Upper Cretaceous-Lower Tertiary sediments in Quseir-Safaga district.

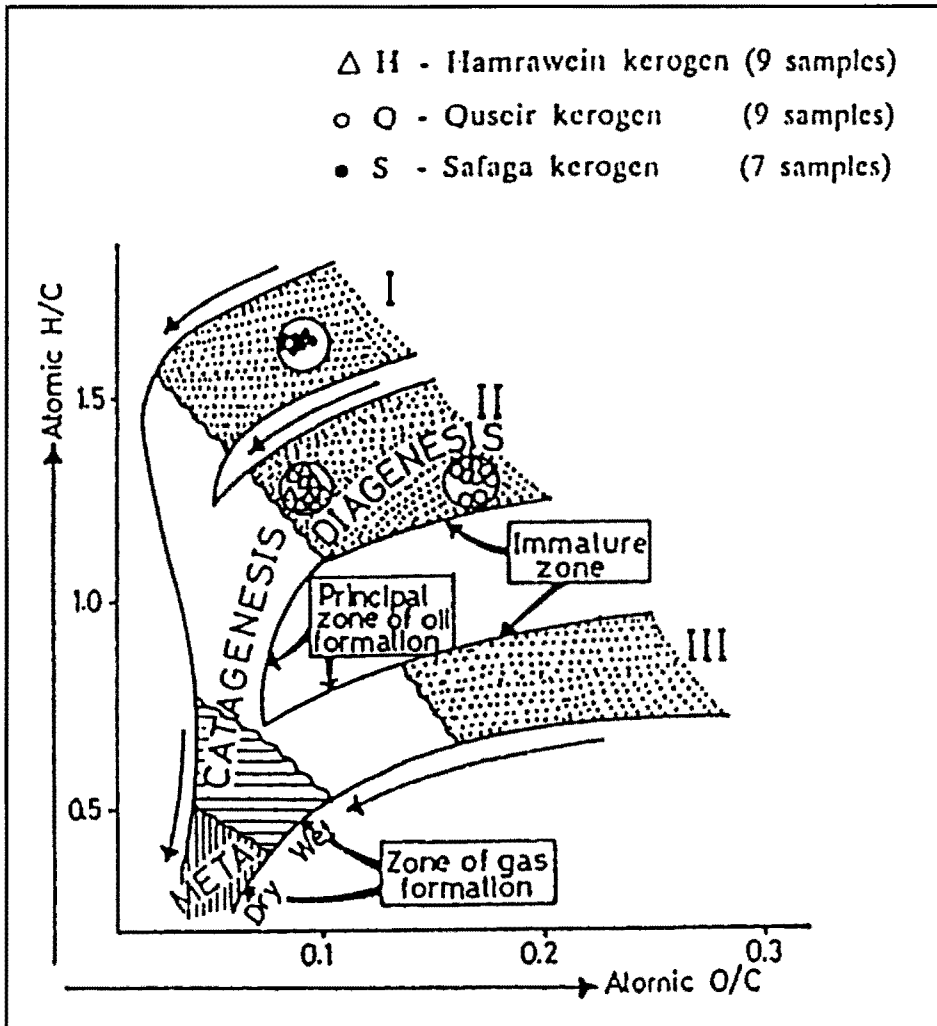


Fig. 4. The elemental analysis results of kerogens of the studied oil shales plotted on van Krevelen diagram (After Khaled, 1992a).

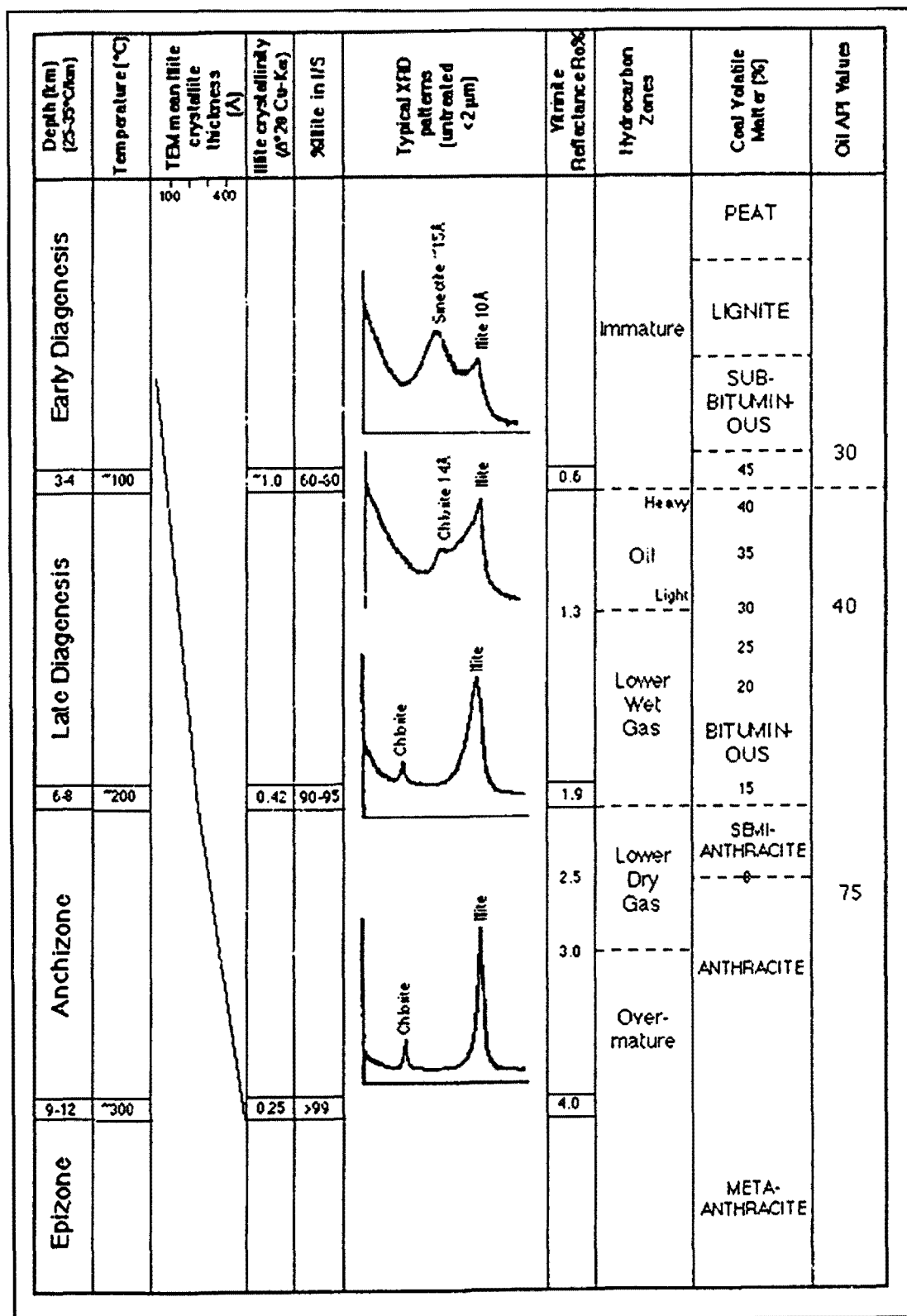


Fig. 5. Basin maturity chart for clay minerals and organic materials (After Merriman, Kemp and Smith, 1995).